

Shuttle inhibitor effect of lithium perchlorate as an electrolyte salt for lithium–sulfur batteries

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Abstract Lithium perchlorate (LiClO_4), used as an electrolyte salt for lithium–sulfur batteries, has been shown to give rise to the effective inhibition of the chemical polysulfide shuttle and thereby to enhance the coulombic efficiency through the stabilized charge process. In 1,2-dimethoxy ethane (DME)/1,3-dioxolane (DOL) (50:50 by volume), LiClO_4 showed the lowest charge-transfer resistance among the various lithium salts studied and demonstrated the highest coulombic efficiency with an extreme reduction in the polysulfide shuttle. The origin of this behavior is considered to be the rapid formation of a passivation layer on the surface of the lithium metal anode. Hence, as well as being a good electrolyte salt in itself, LiClO_4 is shown to be an effective polysulfide shuttle inhibitor.

Keywords Polysulfide shuttle · Inhibitor · Passivation layer · Lithium salts · Lithium–sulfur battery

1 Introduction

Lithium–sulfur batteries are considered to be very attractive power sources because of their high energy densities [1–3], and sulfur is regarded as one of the best candidate cathode materials for rechargeable lithium metal batteries because of its high theoretical specific capacity of $1,675 \text{ mAh g}^{-1}$

and its theoretical energy density of $2,600 \text{ Wh kg}^{-1}$ in the lithium–sulfur battery. Lithium–sulfur batteries are now being widely studied by many research groups, with the purpose of taking advantage of their high energy densities in comparison with lithium–ion batteries [4–6]. Although lithium–sulfur cells have many advantages, their capacity utilization and cyclic stability remain severe problems because of the loss of the sulfur active material and dendrite formation on the lithium anode surface. In particular, one of the most serious problems in lithium–sulfur batteries is the extremely long charging process without any potential increase; this is due to the interaction between lithium (poly)sulfide and lithium metal on the anode, which is called the polysulfide shuttle. Much effort has therefore been made to solve this problem by changing the electrolyte composition or by including some additives [7–10].

In this study, we focus on the effect of the lithium salt on the shuttle problem. It has been reported that a mixed solvent of ether and a cyclic solvent has a high ionic conductivity, good polysulfide solubility, high electrochemical stability, and good chemical compatibility with lithium metal and is also safe to use [11–18]. On the basis of previous studies, we fixed the electrolyte solvent with 1,2-dimethoxy ethane (DME) and 1,3-dioxolane (DOL). Then, various lithium salts such as LiCF_3SO_3 (LiTF), $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (LiTFSI), and LiClO_4 were dissolved, and these solutions were evaluated in terms of their ionic conductivities, viscosities, charge-transfer resistances, and finally, their charge/discharge properties.

2 Experimental

The lithium salts used were LiCF_3SO_3 (LiTF), $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (LiTFSI), and LiClO_4 and were purchased from Aldrich and

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used without pretreatment. The electrolytes used were made up of 1 M lithium salts in solvent mixtures of DME (Aldrich, 98%) and DOL (Aldrich, 98%) with different volume ratios. The volume ratios of DME/DOL were varied as 100:0, 80:20, 67:33, 50:50, 33:67, 20:80, and 0:100. The sulfur cathode consisted of 70 wt% elemental sulfur as the active material (Aldrich, 100 mesh, 99%), 15 wt% Denka Black as the conductor, and 15 wt% poly(vinylidene fluoride) as the binder. The ionic conductivities of the electrolytes were measured using a conductivity meter (Metrohm 856, Tiamo) in a dry room (dew point: $-60\text{ }^{\circ}\text{C}$) at room temperature. The morphologies of the lithium anodes were examined by scanning electron microscopy (SEM, Hitachi S-4200). The elements at the surface of the lithium electrode were analyzed by energy-dispersive spectrometry (EDS, Hitachi S-4200). AC impedance measurements were performed over the frequency range 1 MHz–0.1 Hz using a Solartron 1260 frequency response analyzer coupled with a 1,286 electrochemical interface with a Li/electrolyte/Li cell. The AC amplitude used during the measurements was 5 mV. Lithium–sulfur cells were assembled using a microporous polypropylene separator (Celgard 2400) soaked in the abovementioned electrolyte, the sulfur cathode, and the lithium metal anode in a CR2032 coin cell. Cycle tests were conducted for these cells in the voltage range 1.5–2.8 V versus Li/Li⁺ by the constant-current method using a Maccor cycle system (S 4000, USA).

3 Results and discussion

The changes in ionic conductivity of the DME/DOL-based binary electrolytes with various lithium salts (1 M concentration) can be seen in Fig. 1a. LiClO₄ was wholly dissolved in the various compositions of the DME/DOL solvent, except for pure DME, in which the salt precipitated at 25 °C. LiTFSI and LiTF were perfectly dissolved in all compositions of the DME/DOL solvent. Of the various ratios of DME/DOL, the highest ionic conductivities were observed in the DME/DOL volume ratio of 50:50 for both the 1 M LiTFSI and 1 M LiClO₄ lithium salts. The ionic conductivity of an electrolyte is generally governed by the degree of ionic concentration and mobility. The dielectric constants of the DME and DOL solvents are 7.20 and 7.13, respectively, at 25 °C [19]. This indicates that these solvents have similar capabilities for the dissociation of lithium salts. Therefore, the high ionic conductivities of 1 M LiTFSI and 1 M LiClO₄ are attributable to the increased ionic mobility, irrespective of the concentration of dissociated lithium ions in the DME/DOL-based binary solvents.

Figure 1b shows the changes in the charge-transfer resistances of the DME/DOL-based binary electrolytes with various lithium salts (1 M concentration) from the

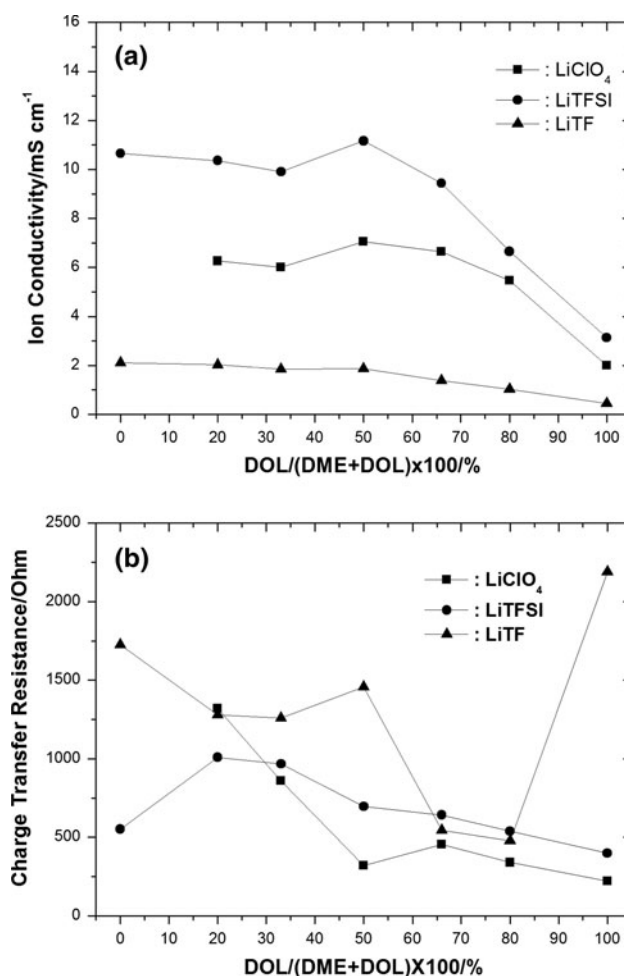


Fig. 1 **a** Ionic conductivity and **b** charge-transfer resistance of various electrolytes as a function of DME/DOL ratio

impedance results at the initial state. In general, the addition of the DOL component improves the charge-transfer resistance. The DME component could give a good charge/discharge reaction of lithium–sulfur battery because of its high solubility to polysulfide [13]. In the case of the LiClO₄ lithium salt, the charge-transfer resistance decreased dramatically at a DME/DOL volume ratio of 50:50, and it showed the lowest value among the various lithium salts. This result indicates that LiClO₄ reacts most rapidly with lithium metal and promptly forms a passivation layer on the surface. The above results on the charge-transfer resistance were obtained from electrochemical impedance spectroscopy (EIS) with the Li/electrolyte/Li cell, as shown in detail in Fig. 2.

The charge/discharge voltage profiles of the lithium–sulfur batteries based on the 1 M LiClO₄, 1 M LiTF, and 1 M LiTFSI electrolytes with a 50:50 volume ratio of DME/DOL are shown in Fig. 3. There are two distinct potential plateaus at about 2.2 and 1.95 V versus Li/Li⁺ during the discharge of the lithium–sulfur battery. The first

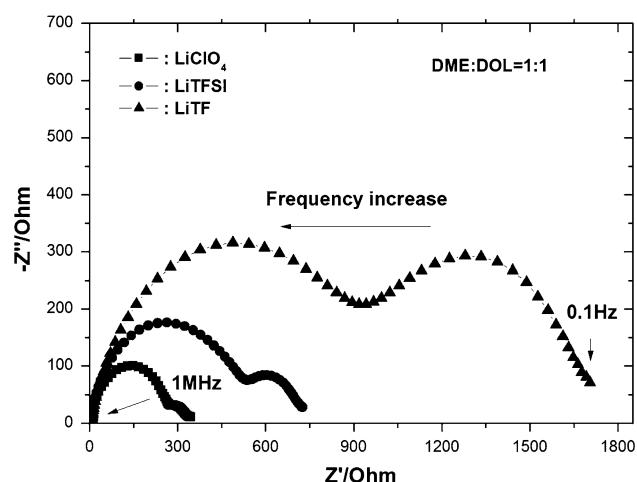


Fig. 2 The impedance plots of Li/electrolytes/Li cell at initial state under open-circuit potential

potential corresponds to the reduction of sulfur to soluble polysulfide and the second to the reduction of polysulfide to a solid reduction product such as Li_2S_2 or Li_2S . The initial specific discharge capacities were nearly 1,000, 850, and 750 mAh g^{-1} for LiTFSI, LiTF, and LiClO_4 , respectively. After 20 cycles, the first plateau potential at 2.2 V almost disappeared, while the second plateau potential increased to 2.1 V versus Li/Li^+ , and showed a similar specific discharge capacity of 500 mAh g^{-1} irrespective of the type of lithium salt. The charge curves of these batteries also each exhibited two plateaus. However, a similar specific discharge capacity (about 500 mAh g^{-1}) was obtained irrespective of the type of lithium salt. It is interesting to note that the patterns of the charge/voltage curves varied greatly depending on the lithium salt. The width of the higher potential plateau varied in the following order: $\text{LiTF} > \text{LiTFSI} > \text{LiClO}_4$. This order is perfectly consistent with the order of charge-transfer resistance shown in Fig. 1b. Since the long plateau region in the charging process is due to the chemical polysulfide shuttle, which is the re-oxidation of reduced lithium sulfide at the cathode, this result indicates that LiClO_4 is the most effective shuttle inhibitor. This can be elucidated from the fact that LiClO_4 showed the lowest charge transfer.

Figure 4 shows the surface structure of the lithium anode before and after the first cycle in the various electrolytes. It is observed that the lithium anode cycled in the 1 M LiClO_4 electrolyte was quite smooth and dense compared with those in the other electrolytes. EDS was applied to identify the elements on the surface of the lithium electrode after 20 cycles, and the results are summarized in Table 1. The sulfur content on the lithium anode increased dramatically in the 1 M LiClO_4 electrolyte after cycling, indicating the formation of a passivation layer of Li_2S_2 and Li_2S .

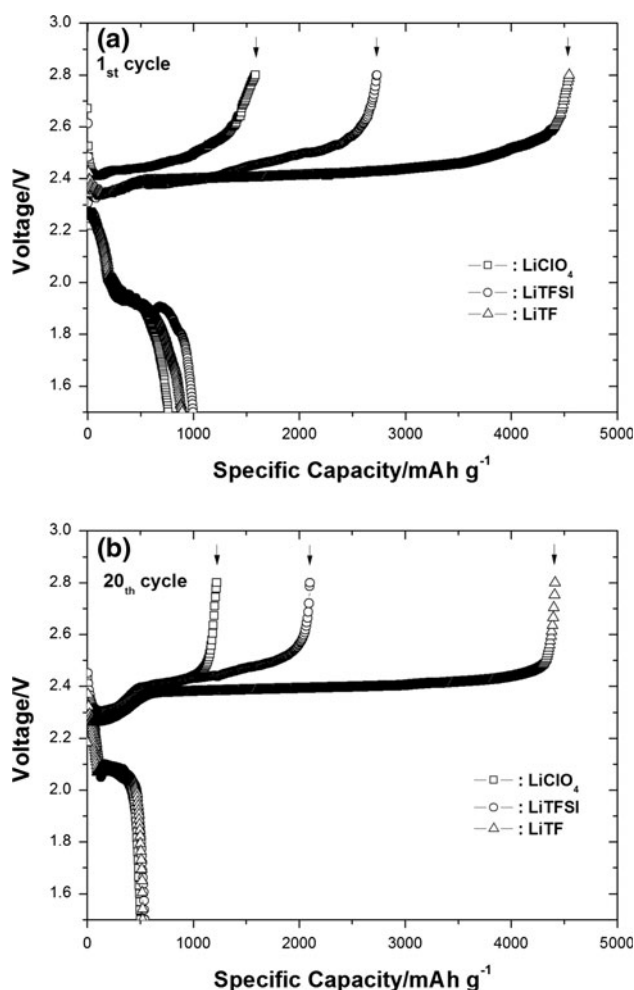


Fig. 3 Charge/discharge voltage curves in **a** 1st cycle, and **b** 20th cycle of lithium-sulfur batteries at 0.1C rate in 1 M LiTFSI, LiTF, and LiClO_4 electrolytes (DME/DOL = 50:50)

It is widely recognized that the formation of a passivation layer on the lithium metal surface can effectively inhibit the formation of lithium dendrites and thereby stabilize the cell performance [20]. In particular, LiNO_3 has been considered one of the most effective additives for the formation of this passivation layer in lithium metal batteries [10]. Hackerman et al. [21] reported that the perchlorate anion has a similar passivation potential to the nitrate anion for any pH examined. In addition, Takehara et al. [22] showed that LiClO_4 and LiPF_6 directly reacted with the lithium metal surface and rapidly formed a dense passivation layer of LiCl or LiF , respectively. Hence, it is naturally expected that LiClO_4 may also effectively form a passivation layer on the surface of the lithium metal. Furthermore, the lowest charge-transfer resistance leads to the fastest formation of the passivation layer among the lithium salts used. The origin of the effective inhibition of the polysulfide shuttle is therefore the employment of LiClO_4 , which shows desirable passivation layer formation, thus

Fig. 4 SEM images of the lithium anodes before (a) and after cycled in LiClO_4 (b), LiTFSI (c), and LiTF (d) electrolytes

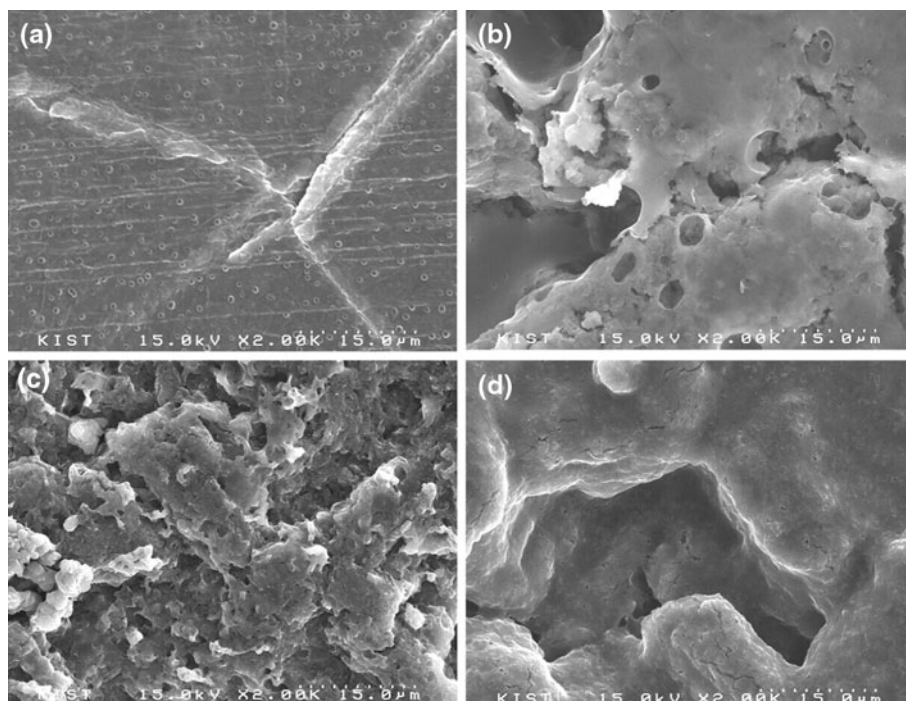


Table 1 Sulfur content on the lithium electrode in various electrolytes

Electrolytes	1 M LiClO_4 (%)	1 M LiTFSI (%)	1 M LiTF (%)
1st cycle	5.30	6.03	4.77
20th cycle	23.24	8.50	3.83

preventing the re-oxidation of polysulfide at the anode surface. Even though LiPF_6 , which can form a denser passivation layer (mainly LiF) on the lithium metal surface than LiClO_4 , can lead to more effective shuttle inhibition, it is impossible to employ this compound as the electrolyte salt because of its insolubility in the DME/DOL system.

Figure 5 shows the cycling performances of lithium–sulfur batteries based on the 1 M LiClO_4 , 1 M LiTF , and 1 M LiTFSI electrolytes with a DME/DOL volume ratio of 50:50. The specific discharge capacities decreased for the initial five cycles with all types of lithium salts. After five cycles, these cells exhibited specific discharge capacities of 550 mAh g^{-1} without further capacity fading. Consequently, even though little difference was shown in the cycling performance, the coulombic efficiency clearly varied for the different lithium salts, which determined the surface condition of the lithium metal and thereby the shuttle transfer in the charging process. In the case of the 1 M LiClO_4 electrolyte with 0.2 M LiNO_3 as an additive, the coulombic efficiency was almost 100% during cycling.

Figure 6 shows the rate capability of the lithium–sulfur battery based on the 1 M LiClO_4 electrolyte in the first

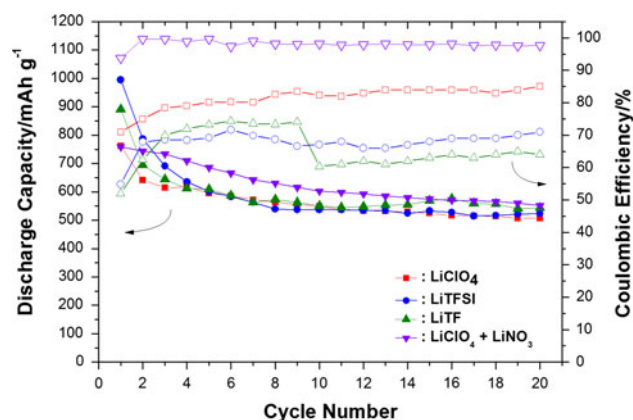


Fig. 5 Cycling performances of lithium–sulfur batteries at 0.1C rate in 1 M LiTFSI , LiTF , LiClO_4 , and 1 M LiClO_4 + 0.2 M LiNO_3 electrolytes (DME/DOL = 50:50)

discharge process. Although the average working discharge voltages were low at high current drains, the specific discharge capacity of the lithium–sulfur battery decreased slightly up to the 0.5C rate and was about 720 mAh g^{-1} even at the 1C rate. This revealed the high utilization of the sulfur together with a low overpotential at high rates. Figure 7 shows the cycling performance of the lithium–sulfur battery based on the 1 M LiClO_4 electrolyte at the 1C rate. The battery still maintained 80% of the initial capacity up to 50 cycles. This stabilized cycling performance may be attributed to the protective passive film formed on the surface of the lithium anode. This film benefits the transfer of lithium ions and plays a role in

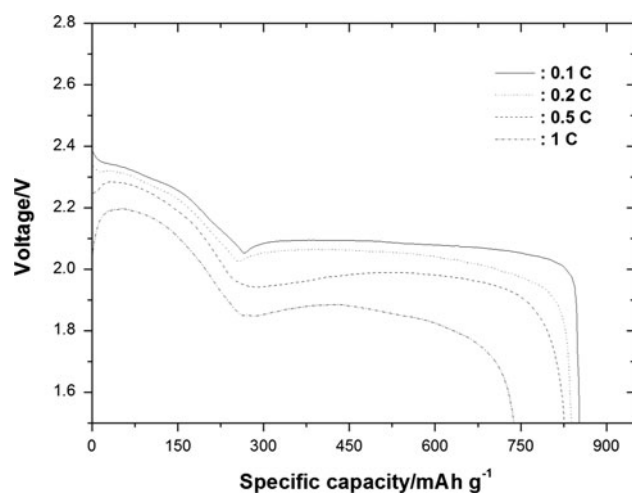


Fig. 6 Rate capability of lithium–sulfur battery at the first discharge process in 1 M LiClO_4 electrolyte (DME/DOL = 50:50)

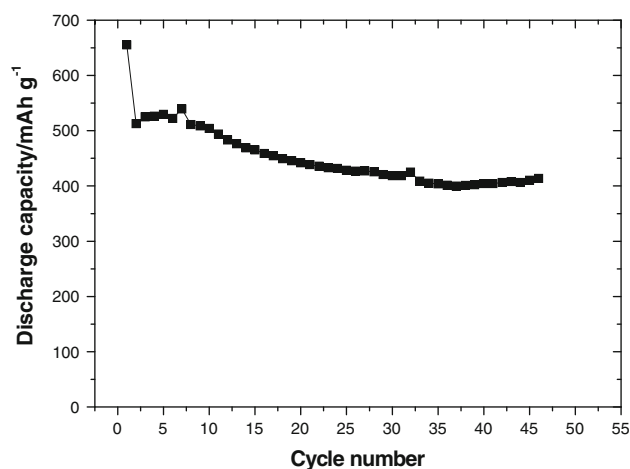


Fig. 7 Cycling performances of lithium–sulfur batteries at 1C rate in 1 M LiClO_4 electrolyte (DME/DOL = 50:50)

preventing the shuttle reaction between the high-ordered polysulfides and the lithium electrode.

4 Conclusions

The effect of lithium salts on the polysulfide shuttle problem was investigated in binary electrolytes based on DME and DOL for lithium–sulfur batteries. The lithium salts were found to affect the ionic conductivity of the electrolyte as well as the charge-transfer resistance. A DME/DOL volume ratio of 50:50 was identified as the

best composition for all the lithium salts in view of the ionic conductivity and charge transfer. In particular, LiClO_4 , having the lowest charge-transfer resistance, showed a dramatically increased coulombic efficiency. This was because the polysulfide shuttle problem was reduced by the rapid formation of a dense passivation layer. Hence, the employment of LiClO_4 , playing the roles of both the lithium salt and the shuttle inhibitor, enables us to obtain a good performance and a stabilized charge process in lithium–sulfur batteries.

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